Inorg. Chem. **1984**, *23*, 4533-4538

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Ligand Effects on the Excited-State Dynamics of Rhodium(III) Complexes: Photoluminescence Properties of the Tetraammine Complexes $Rh(NH_3)_4XY^{n+}$ and Their Relationship to Photoreactivity

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Received April 11, 1984

Reported are the emission spectra and excited-state lifetime data for the series of tetraamminerhodium(III) complexes *cis*- and *trans*-$[Rh(NH_3)_4XY^{n+}]$ ($X = Cl^-, Br^-, H_2O$; $Y = X, H_2O, OH^-$) in 77 K 4/1 methanol/water glasses. Luminescence in each case is a broad Gaussian band assigned as ligand field phosphorescence. Also reported are room-temperature phosphorescence lifetimes for those complexes with $X = Cl^-, Br^-$, $Y = X, H_2O, OH^-$ in aqueous solutions. The latter data are combined with photoreaction quantum yield values to calculate rate constants for the excited-state substitution reactions. From these data it is shown that the influences of Y on the rates of X aquation ($X = Cl^-, Br^-$) from the LF excited state follows the approximate order cis X > trans OH^- ≈ trans X > NH_3 ≈ cis OH^-. These data are discussed in terms of the proposed dissociative mechanism for the excited-state substitution reaction.

Introduction

Ligand substitution is the most common unimolecular chemical reaction by which electronically excited transition-metal complexes undergo deactivation.[4] Although substitution reactions can be identified as arising from several different types of excited states (ES), the major role of ligand field (LF) states in such photochemistry has been long recognized. The penta- and tetraammine complexes of rhodium(III) have provided valuable models for the study of the photosubstitution mechanisms of hexacoordinate d^6 complexes.[5] For such complexes, the substitution reactions induced by ligand field photoexcitation can largely be attributed to reactions from the lowest energy excited state(s), which are triplet LF states. In order to elucidate the mechanisms of reactions originating from specific excited states, it is particularly valuable to probe the dynamics of key excited-state processes as functions of systemic parameters. This has yet been done for only a few metal complexes. Among these are several rhodium(III) pentaammine complexes, $Rh(NH_3)_5X^{n+}$, for which quantum yields and lifetimes have been measured in various media and under various conditions including those used to determine photosubstitution quantum yields.[6] Under the latter conditions, the kinetics of the deactivation processes of a vibrationally relaxed, electronic excited state can be analyzed according to the following relationship between quantum yields and the rate constants for deactivation:[6b]

$$\Phi_i = \Phi_{ic}\frac{k_i}{k_p + k_n + k_r} \qquad (1)$$

In eq 1 Φ_i is the quantum yield for a particular photoreaction or photophysical process, k_i is the ES rate constant for that process, Φ_{ic} is the efficiency for the internal conversion/intersystem from states populated by initial excitation, k_p is the rate constant(s) for the substitution reactions to give products, and k_n and k_r are the rate constants for nonradiative and radiative deactivation to the ground state. Reported here are both low-temperature (77 K) and ambient-temperature investigations of the photophysical properties of a collection of tetraamminerhodium(III) complexes and calculations of the rate constants for the LF excited-state substitution reactions. These studies allow one to evaluate ligand and stereochemistry effects on the dynamics of the photochemical and photophysical processes.

The tetraammine complexes *cis*- and *trans*-$Rh(NH_3)_4XY^{n+}$ ($X = Cl^-, Br^-, OH^-, H_2O$; $Y = X, OH^-, H_2O, NH_3$) have special significance because they have been found to undergo photoisomerizations in conjunction with the ligand photolabilizations (e.g., eq 2 and 3).[7-9] Thus, it is also of interest

$$cis\text{-}Rh(NH_3)_4Cl_2^+ + H_2O \xrightarrow{h\nu} Rh(NH_3)_4(H_2O)Cl^{2+}\ (17\%\ trans,\ 83\%\ cis) + Cl^- \qquad (2)$$

$$trans\text{-}Rh(NH_3)_4(OH)Cl^+ + OH^- \xrightarrow{h\nu} Rh(NH_3)_4(OH)_2^+\ (>90\%\ cis) + Cl^- \qquad (3)$$

to examine whether there is any correlation between the tendencies to undergo photoisomerization and the LF ES energies or lifetimes.

Experimental Section

Materials. The amminerhodium(III) complexes $[Rh(NH_3)_5Br]Br_2$,[10] *cis*-$[Rh(NH_3)_4X_2]X\cdot{}^1/_2H_2O$,[11] *trans*-$[Rh(NH_3)_4X_2]X\cdot H_2O$,[12]

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Table I. Emission and Absorption Data for Tetraamminerhodium(III) Complexes

	emission properties[g]				
complex	τ,[a] μs	ν_{max}, μm^{-1}	$\Delta\nu_{1/2}$, μm^{-1}	ν_{0-0}, μm^{-1}	ν_{max}(abs[b]), μm^{-1}
$[Rh(NH_3)_5Cl](ClO_4)_2$[c]	12.2	1.50	0.28	1.86	2.89
trans-$[Rh(NH_3)_4Cl_2]Cl\cdot H_2O$	7.6	1.36	0.25	1.68	2.41
cis-$[Rh(NH_3)_4Cl_2]Cl\cdot {}^1/_2H_2O$	0.7	1.31	0.29	1.68	2.78
trans-$[Rh(NH_3)_4(H_2O)Cl](ClO_4)_2$	0.7	1.29	0.29	1.66	2.57
cis-$[Rh(NH_3)_4(H_2O)Cl](ClO_4)_2$	0.5[d]				2.87
trans-$[Rh(NH_3)_4(OH)Cl]^{+}$[e]	3.5	1.43	0.27	1.78	2.69
$[Rh(NH_3)_5Br](ClO_4)_2$	10.3	1.49	0.27	1.84	2.79
trans-$[Rh(NH_3)_4Br_2]Br\cdot H_2O$	7.7	1.34	0.25	1.68	2.27
cis-$[Rh(NH_3)_4Br_2]Br\cdot {}^1/_2H_2O$	1.0	1.30	0.27	1.66	2.65
trans-$[Rh(NH_3)_4(H_2O)Br](ClO_4)_2$	0.7	1.23	0.27	1.57	2.46
cis-$[Rh(NH_3)_4(H_2O)Br](ClO_4)_2$	0.6	1.30	0.29	1.67	2.75
trans-$[Rh(NH_3)_4(OH)Br]^{+}$[e]	6.1	1.45	0.22	1.74	2.62
cis-$[Rh(NH_3)_4(OH)Br]^{\bullet}$[e]	5.0	1.44	0.23	1.73	2.75
$[Rh(NH_3)_5(H_2O)](ClO_4)_3$[f]	2.7	1.49	0.32	1.90	3.17
trans-$[Rh(NH_3)_4(H_2O)_2](ClO_4)_3$	nonexp	1.45	0.28	1.81	2.83
cis-$[Rh(NH_3)_4(H_2O)_2](ClO_4)_3$	0.2	1.40	0.29	1.77	3.07
trans-$[Rh(NH_3)_4(H_2O)(OH)]S_2O_6$	nonexp	1.34	0.29	1.72	2.88
cis-$[Rh(NH_3)_4(H_2O)(OH)]S_2O_6$	5.0	1.44	0.30	1.83	3.04

[a] Precision on lifetime measurements ±20% or better, except where noted; nonexp = nonexponential decay. [b] In 298 K aqueous solution, lowest energy (singlet) LF absorption band listed. Data from ref 11–13 plus: Jørgensen, C. K. *Acta Chem. Scand.* 1956, *10*, 500. [c] Emission data from ref 16. [d] Emission very weak. [e] Dithionate salt of aquo complex dissolved in alkaline solution. [f] Emission data from ref 17. [g] Conditions: 4/1 CH_3OH/H_2O; 77 K.

cis- and *trans*-$[Rh(NH_3)_4(H_2O)X]S_2O_6$, X = Cl^-, Br^-,[7a] *cis*- and *trans*-$[Rh(NH_3)_4(H_2O)_2](ClO_4)_3$,[13] and *cis*- and *trans*-$[Rh(NH_3)_4(H_2O)(OH)]S_2O_6$[13,14] were all made and purified by published procedures. Other chemicals were of analytical grade, and doubly distilled water was used throughout. The *cis*- and *trans*-$[Rh(NH_3)_4(H_2O)X]S_2O_6$ salts were recrystallized as perchlorates for the measurement in glasses at 77 K to enhance their solubilities in 4/1 CH_3OH/H_2O solutions. The recrystallizations were performed by dissolving the dithionate salts in a minimum of hot water and adding an equal volume of 70% $HClO_4$. After the solutions were cooled at 5 °C for several hours, the perchlorate salts were collected on sintered-glass filters and washed with ethanol and then with ether.

Emission Spectra and Emission Lifetimes. The 77 K emission spectra and emission lifetimes were measured with use of the third harmonic (355 nm) of a Quanta Ray DCR-1A Nd(YAG) laser system as the excitation source. Samples were investigated as solutions in 4/1 CH_3OH/H_2O glasses in 2 cm diameter cylindrical Pyrex emission tubes. An optical Dewar held the sample tube in liquid nitrogen. The emissions were monitored at right angles through a Perkin-Elmer Model 98 monochromator using an EMI 9816A, and EMI 9558QA, or a dry-ice-cooled EMI 9808B photomultiplier tube as detector. The emission spectra were obtained at 10 Hz with the monochromator scanning in wavelength and with a PAR Model 162 boxcar averager and a Model 164 integrator. The averaged signal was rendered on a strip-chart recorder. For the emission lifetimes, the emission intensities at selected wavelengths were monitored and the output of the photomultiplier was displayed on a Tektronix 7904 oscilloscope.

The emission lifetimes and spectra at 298 K were measured in dilute acidic aqueous solutions (10^{-3} M $HClO_4$) at 298 K by single-photon correlation techniques with a mode-locked argon ion laser as described previously.[15] This laser produces pulses of about 200-ps duration at a repetition rate of 82 MHz when tuned to the wavelength 458 nm, which corresponds in each case to the long-wavelength tail of the ligand field absorption. Sample photolysis was a problem in some cases, so flow cells were used and total irradiation times were limited to 200 s/sample except in the cases of photoinactive complexes.

Results

Emission spectra and lifetimes were measured for the various rhodium(III) ammine complexes under two sets of conditions: at 77 K in aqueous methanol glasses and at 298 K in dilute aqueous solutions. For the low-temperature experiments, the observed luminescence spectrum in each case was a broad Gaussian band such as has been described previously for the halopentaammine complexes $Rh(NH_3)_5X^{2+}$, X = Cl^-, Br^-, I^-.[6,16] The ν_{max} values from the corrected emission spectra and the measured lifetimes for these low-temperature experiments are listed in Table I. Also listed are the band widths at half height ($\nu_{1/2}$) and estimates of the 0–0 energies (ν_{0-0}) for the emitting excited state as calculated from eq 4.[6a]

$$\nu_{0-0} = \nu_{max} + 1.29\nu_{1/2} \qquad (4)$$

In comparison to the halopentaammine complexes (Table I), the various tetraammines are all weak emitters; thus, relatively high complex concentrations (20–50 mg/10 mL of solvent) were initially used to provide moderate signals for the spectral recording and lifetime measurements in the low-temperature glasses. However, a persistent problem with nonexponential emission decay was found for a number of these species. Furthermore, while such nonexponential decays could be analyzed as sums of two or more first-order decay processes in the microsecond time frame, the relative contributions of these decays for a particular compound would change from experiment to experiment. This phenomenon was investigated in detail for the bromopentaammine complex $[Rh(NH_3)_5Br]Br_2$, which was a much stronger emitter and which had been reported as displaying a single exponential decay under these conditions.[15] For this complex, reproducible, simple first-order decay curves with lifetimes in agreement with those reported were observed for concentrations of the salt less than 10 mg/10 mL of the aqueous methanol solutions. However, for the solutions of higher concentrations (15–50 mg/10 mL), significantly nonexponential decay curves, with the new component having a longer lifetime, were consistently found. Similarly, for the tetraammines higher concentrations led to greater contributions from longer lived component(s). Although the specific cause of this phenomenon was not identified, logical candidates would be either ion pairing in solution or the formation of microcrystals too small to observe visually in the (cracked) frozen glasses. In accord with the latter proposal is the observation that emission lifetimes for some of these complexes investigated as solid salts dispersed in KBr pellets[17-19] generally had longer lifetimes than for the same

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Table II. Luminescence Lifetimes and Photochemical Data for the Tetraamminerhodium(III) Complexes $Rh(NH_3)_4XY^{n+}$ in 298 K Aqueous Solution

complex[a]	τ,[b] ns	Φ_{sub}[c]	Φ_{isom}[d]	$10^{-7} \times k_{sub}$,[e] s^{-1}
$Rh(NH_3)_5Cl^{2+}$	14.2	0.19		1.3
trans-$Rh(NH_3)_4Cl_2^+$	1.8	0.14	0.025	7.8
cis-$Rh(NH_3)_4Cl_2^+$	1.3	0.40	0.33	31.0
trans-$Rh(NH_3)_4(H_2O)Cl^{2+}$	2.2	0.40	0.074	18.0
cis-$Rh(NH_3)_4(H_2O)Cl^{2+}$	2.4	0.66	0.54	28.0
trans-$Rh(NH_3)_4(OH)Cl^+$	2.7	0.21	0.21	7.8
cis-$Rh(NH_3)_4(OH)Cl^+$	3.2	~0.02	<0.01[f]	~0.6
$Rh(NH_3)_5Br^{2+}$	13.0	0.20	[g]	1.5
trans-$Rh(NH_3)_4Br_2^+$	1.5	0.10	[g]	6.6
cis-$Rh(NH_3)_4Br_2^+$	1.0	0.30	⩽0.24	30.0
trans-$Rh(NH_3)_4(H_2O)Br^{2+}$	1.7	[h]	[h]	[h]
cis-$Rh(NH_3)_4(H_2O)Br^{2+}$	1.6	⩾0.50[i]	0.50	⩾31.0[i]
trans-$Rh(NH_3)_4(OH)Br^+$	2.3	0.33	0.33	14.0
cis-$Rh(NH_3)_4(OH)Br^+$	2.1	~0.02	<0.01[f]	~1.0

[a] In dilute aqueous solution. [b] Phosphorescence lifetimes, see Results; experimental precision ±25% or better in each case. Data from ref 6b, 20 and this work. [c] Total quantum yield for substitution reactions in mol/einstein; i.e. $\Phi_{sub} = \Phi_X + \Phi_{NH_3} + \Phi_{H_2O}$. Data from ref 6d, 7a–e. $\lambda_{irr} = 366$ nm. [d] Quantum yield in moles/einstein for isomerization (cis → trans or trans → cis) of the tetraammine fragment. Data from ref 7a–e. $\lambda_{irr} = 366$ nm. [e] Total rate constant for substitution reactions of the lowest energy LF triplet state $k_{sub} = \Phi_{sub}\tau^{-1}$; see Discussion. [f] No isomerization was detected. [g] Stereochemistry of product mostly trans, although a minor fraction of the cis product has been detected.[26] [h] H_2O exchange not determined; however, a quantum yield of ~0.4 would be expected from the result seen for *trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$. [i] H_2O exchange has not been investigated for this case; however, the results found for the chloro analogue[7d,e] suggest $\Phi_{H_2O} \geqslant \Phi_{isom}$. However, since the upper limit for Φ_{H_2O} would be 1.0, k_{sub} must have a value $\leqslant 6.2 \times 10^8$ s^{-1}.

compound in the aqueous methanol glasses at the same temperature. Although for some of the weaker emitters this problem could not be altogether avoided, for the cases listed in Table I the major emission component could be easily identified and the lifetime determined. However, for *trans*-$Rh(NH_3)_4(H_2O)_2^{3+}$ and *cis*-$Rh(NH_3)_4(OH)Cl^+$ there was sufficient ambiguity in this regard that no lifetimes are reported.

Qualitatively, the intensities of emission followed the order $Rh(NH_3)_5X^{2+}$ >> *trans*-$Rh(NH_3)_4X_2^+$ > *cis*-$Rh(NH_3)_4X_2^+$ > *trans*-$Rh(NH_3)_4(OH)X^+$ > *cis*-$Rh(NH_3)_4(OH)X^+$ > *cis*- and *trans*-$Rh(NH_3)_4(H_2O)X^{2+}$. Also bromo compounds were generally brighter emitters than the homologous chloro complexes. No emission was found for the dihydroxo complexes *cis*- and *trans*-$Rh(NH_3)_4(OH)_2^+$.

The room-temperature lifetimes for emission from the lowest energy LF triplet states of the tetraammine complexes $Rh(NH_3)_4X_2^+$, $Rh(NH_3)_4(OH)X^+$, and $Rh(NH_3)_4(H_2O)X^{2+}$ (X = Cl^-, Br^-) are summarized in Table II. No room-temperature data could be obtained for the diaquo, dihydroxo, or aquohydroxo tetraammine complexes as these did not absorb sufficiently at the 458-nm excitation wavelength of the picosecond apparatus to give measurable emission. The data for some of these have been reported previously,[15] but only the data for the dibromo complexes have been discussed in the context of the photochemical properties.[20] With the ultrasensitive picosecond laser system necessary to measure the ambient-temperature phosphorescence lifetimes of the tetraammines, the total quantum yields for emission were estimated as being in the range $10^{-7} < \Phi_{em} < 10^{-6}$.[15] In addition, the picosecond system detected two components of the emission profile, a "phosphorescence" displaying the broad Gaussian emission seen at low temperature, and a much shorter lived (<100 ps), apparently temperature independent, higher energy emission, which has been attributed to "fluorescence" from incompletely relaxed LF singlets.[15] The relative contributions of the room-temperature emission components are concentration independent and thus have no relationship to the medium-dependent emission behavior noted above in low-temperature glasses.

Discussion

Low-Temperature Photophysical Properties. The following observations can be drawn from data in Table I for the emissions from the lowest energy LF states of the various $Rh(NH_3)_4XY^{n+}$ complexes. For X = either Cl^- or Br^-, the ν_{max} values follow the order Y = NH_3 > cis or trans OH > trans X > cis X ≈ H_2O. A similar situation is seen with the ν_{0-0} values, which follow the apparent order Y = NH_3 > OH > cis or trans X ≈ H_2O. The differences in either ν_{max} or ν_{0-0} between homologous pairs for X = Br^-, Cl^- are rather small. Perhaps the surprising feature of these data is the rather high ν_{0-0} energies seen for the *cis*- and *trans*-hydroxohalotetraammine $Rh(NH_3)_4(OH)X^+$ especially in analogy to the aquohalotetraammines. Hydroxide is normally considered a weaker field ligand than H_2O (owing to the former's strong π-donor ability, which compensates for its superior σ-donor strength) but for the LF excited states of these tetraammine complexes, the σ-donor ability of the OH^- may play the larger role in determining the ligand field strength.

The 77 K lifetimes of the tetraammine complexes are all much shorter than seen for the halopentaammines with the approximate order Y = NH_3 > trans X ≈ cis or trans OH^- > cis X ≈ cis or trans H_2O for X = Cl^-, Br^-. Again, the lifetime data show little dependence on whether X = Cl^- or Br^- but are sensitive to the nature of and stereochemical position occupied by Y. Comparison of the low-temperature lifetimes (Table I) and the ambient-temperature photosubstitution quantum yields (Table II) indicates a very rough correlation showing that the more photolabile complexes display the shorter lifetimes. This might suggest a strong coupling contribution to the low-temperature nonradiative deactivation pathway,[21] but the correspondence between these data is not exact. Similarly, there is a rough correlation between ν_{max} and ln τ^{-1} (i.e., ~ln k_n given that $\tau = (k_n + k_r)^{-1}$ and $k_n >> k_r$ under these conditions) as suggested by the energy gap law applied to nonradiative decay; however, there are significant deviations from the linear behavior proposed.[22]

An interesting comparison can be made to spectra and lifetime data recorded previously for some of these complexes in the solid state (as 2% KBr pressed pellets).[18] The lifetime and the ν_{max} values for $[Rh(NH_3)_5X]X_2$ or *trans*-$[Rh(NH_3)_4X_2]X$ in the KBr pellets are essentially identical with those in the aqueous methanol glasses at 77 K. However, for the [*cis*-$Rh(NH_3)_4X_2$]X salts the situation is different. The values τ = 2.3 ns, ν_{max} = 1.42 μm^{-1} (X = Cl^-) and τ = 2.2 ns, ν_{max} = 1.41 μm^{-1} (X = Br^-) were measured in the KBr pellets,[18] the lifetimes significantly longer and the ν_{max} values significantly higher than found for these compounds in frozen solution. Given that the partial molar volumes measured for the *cis*-dihalo complexes in aqueous solution are ~18 cm^3/mol smaller than those found for the trans isomers,[7g] the greater medium dependence of the cis-isomer photophysical properties may reflect some specific solvation phenomena in these cases.

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Table III. Quantum Yields for Photosubstitution Reactions and Calculated Rate Constants for Deactivation Processes of the LF States in 298 K Aqueous Solution

complex	Φ_X[a]	Φ_{NH_3}[a]	Φ_{H_2O}[a]	k_X[b]	k_A[b]	k_{H_2O}[b]	k_n[c]
$Rh(NH_3)_5Cl^{2+}$	0.15	0.04		1.1 ± 0.1	0.28 ± 0.07	...	5.7 ± 0.5
trans-$Rh(NH_3)_4Cl_2^+$	0.14	$\leq$0.002		8 ± 1	$\leq$0.11	...	48 ± 10
cis-$Rh(NH_3)_4Cl_2^+$	0.39	0.013		30 ± 6	1.0 ± 0.2	...	46
trans-$Rh(NH_3)_4(H_2O)Cl^{2+}$	$\leq$0.01	$\leq$0.001	0.39	$\leq$0.5	$\leq$0.05	18 ± 5	27
cis-$Rh(NH_3)_4(H_2O)Cl^{2+}$	$\leq$0.01	$\leq$0.001	0.66	$\leq$0.4	$\leq$0.04	28 ± 7	14
trans-$Rh(NH_3)_4(OH)Cl^+$	0.21	*d*		8 ± 2	...	...	29
cis-$Rh(NH_3)_4(OH)Cl^+$	~0.02	*d*		~0.6	...	...	31
$Rh(NH_3)_5Br^{2+}$	0.02	0.18		~0.2	1.4 ± 0.1	...	6.1 ± 0.2
trans-$Rh(NH_3)_4Br_2^+$	0.10	~0.002		6.7 ± 0.7	~0.13	...	60 ± 5
cis-$Rh(NH_3)_4Br_2^\bullet$	0.24	0.06		24 ± 3	6.4 ± 0.8	...	70 ± 10
trans-$Rh(NH_3)_4(H_2O)Br^{2+}$	<0.01	~0.003		<0.6	~0.2	*e*	~35 est[f]
cis-$Rh(NH_3)_4(H_2O)Br^{2+}$	<0.01	~0.006	$\geq$0.50	<0.6	~0.4	$\geq$31	$\leq$31
trans-$Rh(NH_3)_4(OH)Br^+$	0.33	*d*		14 ± 4	...	...	29
cis-$Rh(NH_3)_4(OH)Br^+$	~0.02	*d*		~1.0	...	...	47

[a] Quantum yields for halide (Φ_X), ammonia (Φ_{NH_3}), and water (Φ_{H_2O}) photolabilization of the $Rh(NH_3)_4XY^{n+}$ species in mol/einstein. Data from ref 6d, 7a–e. [b] Rate constants in 10^7 s^{-1} for ligand labilization (k_X, k_{NH_3}, and k_{H_2O}) from the LF excited state calculated from the equation $k_i = \Phi_i \tau^{-1}$; see Discussion. [c] Rate constant in 10^7 s^{-1} for nonradiative deactivation of the lowest energy LF state calculated from the equation $k_n = \tau^{-1} - \Sigma k_p - k_r$; see Discussion. [d] Ammonia aquation quantum yield not determined. [e] Water exchange quantum yield not determined. [f] Estimated; cf. footnote *h* of Table II.

Emission Lifetimes in 298 K Aqueous Solution and Photochemical Implications. As noted in the Results and in a previous report from these laboratories,[15] photoexcitation of the haloamminerhodium(III) complexes in 298 K aqueous solution leads to two emission components, a very fast (picosecond) decay, which was attributed to fluorescence, and a slower (nanosecond) decay, which was attributed to the phosphorescence from a thermally relaxed lowest energy triplet LF state. Despite the very low yield fluorescence, a variety of evidence points to efficient internal conversion/intersystem crossing ($\Phi_{isc} \approx 1$) to the lowest energy LF state from which occurs the bulk of the chemical reactions in competition with nonradiative deactivation.[4,5] If this is the case, the rate constants for different processes from this excited state can be correlated with the measured quantum yields and phosphorescence lifetimes according to eq 5. Similarly, the

$$k_i = \Phi_i \tau^{-1} \tag{5}$$

nonradiative deactivation rate constant can be calculated from eq 6, where $\sum k_p$ is the sum of the first-order reactive deactivation rate constants for that state.

$$k_n = \tau^{-1} - \sum k_p - k_r \tag{6}$$

In this context the radiative rate constant k_r (for phosphorescence) can be estimated. The emission quantum yield is very small with an estimated upper limit of 10^{-6}; thus, given lifetimes of 1–3 ns for the tetraammine complexes in solutions, the upper limit for k_r would be $\sim 10^3$ s^{-1}, a value similar to that measured for the halopentaammine complexes under these conditions.[6b] The nonradiative decay constants (Table III) show one clear trend: k_n is significantly larger for the tetraammine complexes (regardless of stereochemistry) than for the halopentaammine ions. The dihalo ions appear to have systematically larger k_n values than do the aquohalo or hydroxohalo ions of the same halide, but given the experimental uncertainties, the differences are barely significant.

Table III summarizes the values of the rate constants for halide (k_x), ammine (k_A) and water (k_{H_2O}) labilization from the coordination sphere of the complexes in their lowest energy LF excited states. Although the rate constants for ligand labilization are all quite large, some specific patterns of differential lability do clearly emerge.

The lability of a halide ion X^- from the LF excited state (eq 7) will be considered first. The k_x values for the various

$$[Rh(NH_3)_4XY^{n+}]^* + H_2O \rightarrow Rh(NH_3)_4Y(H_2O)^{n+1} + X^- \tag{7}$$

ligands Y follow the order cis $Cl^- >$ trans $OH^- \approx$ trans $Cl^- > NH_3 >$ cis OH^- for $X = Cl^-$ and cis $Br^- >$ trans $OH^- >$ trans $Br^- >$ cis $OH^- > NH_3$ for $X = Br^-$. The role of cis or trans H_2O in terms of labilizing Cl^- or Br^- from the LF state is difficult to evaluate given the uncertainties in the k_x values for these complexes; however, it is clear that halides either cis or trans to H_2O would fall at the low-reactivity end of each series. Interpretation of these rate differences suffers from the complications of changes in the nature and extent of ES distortions as functions of the different complexes. Nonetheless, it can be seen that the introduction of another halide, either cis or trans, markedly accelerates halide labilization. Similar ligand effects have been seen for the ground-state aquation reactions of Co(III) and Rh(III) amine complexes with the parallel observation that the effect is larger when the second halide is in the cis position.[23] The analogy breaks down when the hydroxo complexes are considered. For the thermal aquations, cis or trans hydroxide was shown to have a substantially greater labilizing effect than Cl^- or Br^- in the same stereochemical site.[23] In contrast, while trans OH^- has an ES labilizing effect somewhat larger than that of trans halide (especially if the ES reactivities are normalized by dividing by the number of equivalent halides in the coordination sphere), cis OH^- has little effect relative to NH_3 in the same site. The differences in k_x between *cis*-$Rh(NH_3)_4X_2^+$ and *cis*-$Rh(NH_3)_4(OH)X^+$ very likely are the consequence of different orbital characters of the relevant lowest energy LF states, given that OH^- is a stronger σ donor than is NH_3 while Cl^- is a weaker σ donor.[24]

The position of water in terms of its effects on the k_x values is reasonable, given the similarity to NH_3 in ligand field strength and given the complication that halide aquation is a minor photoreaction pathway for the $Rh(NH_3)_4(H_2O)X^{2+}$ ions compared to the photoexchange of coordinated H_2O with solvent. Notably, the rate constant for the latter reaction (k_{H_2O}) is larger for the *cis*-$Rh(NH_3)_4(H_2O)Cl^{2+}$ ion than for the trans analogue, in accordance with the pattern seen for dichloro complexes.

The ES ammonia aquation rates provide the opportunity to compare the labilization rates of a single ligand for various complexes having different X's (eq 8). To the k_A values of

$$[Rh(NH_3)_4XY^{n+}]^* + H_2O \rightarrow Rh(NH_3)_3(H_2O)XY^{n+} + NH_3 \tag{8}$$

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(23) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions"; Wiley: New York, 1967; Chapter 3.

(24) Glerup, J.; Mønsted, O.; Schaffer, C. E. *Inorg. Chem.* **1976**, *15*, 1389.

Table III can be added the rates for the hexaammine and iodopentaammine complexes[25] to give the following order for k_A: $Rh(NH_3)_5I^{2+}$ > *cis*-$Rh(NH_3)_4Br_2^+$ > $Rh(NH_3)_5Br^{2+}$ > *cis*-$Rh(NH_3)_4Cl_2^+$ > *cis*-$Rh(NH_3)_4(H_2O)Br^{2+}$ > $Rh(NH_3)_5Cl^{2+} \approx Rh(NH_3)_6^{3+}$ > *trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$, *trans*-$Rh(NH_3)_4Br^{2+}$, *trans*-$Rh(NH_3)_4Cl^{2+}$, *cis*- and *trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$. The stereochemical site from which the labilized NH_3 originates has been investigated in but one of these cases (largely, but not exclusively, trans NH_3 aquation from $Rh(NH_3)_5I^{2+}$);[26] however, the reactivity order for k_A suggests the effect of halide in labilizing NH_3 in the ES is largely on the trans position.[27-29] From these data the effect of the ancillary ligand on labilizing NH_3 follows the order $I^- > Br^- > Cl^- \approx NH_3$. The NH_3 labilities are about fourfold larger for the *cis*-dihalo ions $Rh(NH_3)_4X_2^+$ than for the monohalo ions $Rh(NH_3)_5X^{2+}$, but if these rates are normalized to the number of NH_3 groups trans to halide, the effect is only twofold.

An investigation of pressure effects on the ligand field excited-state reaction dynamics of the halopentaammine complexes $Rh(NH_3)_5X^{2+}$ ($X = Cl^-, Br^+$) has led to the conclusion that the probable mechanism for the photosubstitution reactions of these d^6 ions involves limiting dissociative steps,[6e,7g] e.g.

$$[Rh(NH_3)_5X^{2+}]^* \rightarrow [Rh(NH_3)_5^{3+}]^* + X^- \qquad (9)$$

$$[Rh(NH_3)_5X^{2+}]^* \rightarrow [Rh(NH_3)_4X^{2+}]^* + NH_3 \qquad (10)$$

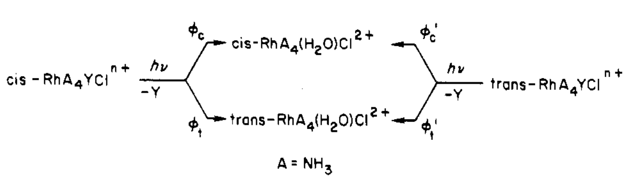
The enhanced ES lability of X^- for the *cis*- and *trans*-dihalotetraammine and the *trans*-hydroxyhalotetraammine complexes is consistent with such a mechanism since dissociation of an anion should be more facile from a monocation than from a dication. The relatively inert character of the *cis*-hydroxohalo complexes tempers this argument, although the logical rationale for this different behavior may lie in the excited-state symmetries.

Strong circumstantial evidence for the limiting dissociative mechanism is provided by the photostereochemistry of the tetraammine ions. Although the analogous thermal reactions are stereoretentive,[23] the photosubstitutions of these complexes are accompanied by considerable stereomobility, e.g., eq 11.[7a]

$$cis\text{-}Rh(NH_3)_4(H_2O)Cl^{2+} \xrightarrow{h\nu} trans\text{-}Rh(NH_3)_4(H_2O)Cl^{2+} \qquad (11)$$

An examination of the reaction depicted in eq 11 using $H_2{}^{18}O$-labeled starting complex has revealed that the photoisomerization ($\Phi_{isom} = 0.54$) is accompanied by photolabilization of the coordinated water with a somewhat higher quantum yield (Table II, $\Phi_{sub}/\Phi_{isom} = 1.22$).[7d] The analogous dichloro ion *cis*-$Rh(NH_3)_4Cl_2^+$ also undergoes photosubstitution/photoisomerization, and while it was originally thought that these pathways had equal yields,[7a] a careful reexamination[7d] has demonstrated that a small amount of the *cis*-$Rh(NH_3)_4(H_2O)Cl^{2+}$ ion is also produced. Thus, the ratio of photosubstitution to photoisomerization is greater than unity ($\Phi_{Cl}/\Phi_{isom} = 1.18$) and is virtually identical with that found for the aquochloro complex. In other words, the two products *cis*- and *trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$ are formed in the identical ratios as the result of the photolabilization of Y from *cis*-$Rh(NH_3)_4YCl^{n+}$ regardless of whether Y is Cl^- or H_2O.

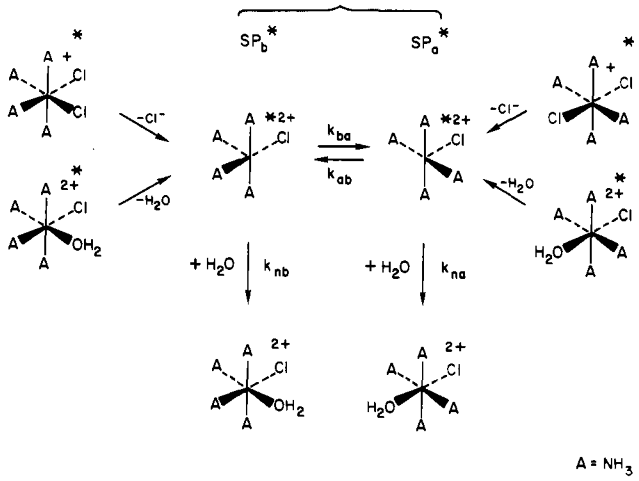
Scheme I



Y	ϕ_c	ϕ_t
$H_2{}^{18}O$	0.12	0.54
Cl^-	0.063	0.33

Y	ϕ_c'	ϕ_t'
$H_2{}^{18}O$	0.074	0.33
Cl^-	0.025	0.122

Scheme II



A careful reexamination of the photochemistry[30] of the *trans*-$Rh(NH_3)_4Cl_2^+$ ion combined with a new study of the photochemistry of the $H_2{}^{18}O$-labeled *trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$ has led to a similar observation.[7e] In these cases modest trans → cis photoisomerization was found to accompany photolabilization, and the Φ_{sub}/Φ_{isom} ratios (5.9 and 5.5, respectively) were found to be very close for the two ions.

It is notable that the ligand field photoaquation of Y from each of the four complexes *cis*- and *trans*-$Rh(NH_3)_4YCl^{n+}$ ($Y = H_2O, Cl^-$) leads to but two products, *cis*- and *trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$. The quantum yields for the formation of these two products are represented in Scheme I and are found to occur in a constant ratio, $\Phi_{cis}/\Phi_{trans} = 0.21 \pm 0.01$ for all starting complexes. Thus, it can be concluded that a common intermediate or a common set of intermediates is formed along the reaction coordinate of all the four photoaquations regardless of the nature of the labilized group Y (H_2O or Cl^-) or initial stereochemistry of the complex (cis or trans).

The theoretical model[7a,8a,31] that very successfully rationalizes these stereochemical results is illustrated in Scheme II. The key assumption is that the LF state of the hexacoordinate complex dissociates one ligand to give an excited-state, square-pyramidal, pentacoordinate intermediate; SP_a^* would be formed from the trans isomers, while SP_b^* would be formed from the cis isomer. Electronic deactivation of SP_a^* followed by trapping by solvent would give the trans product while similar deactivation and trapping of SP_b^* would give the cis product. Rearrangement between these two intermediates provide a pathway for isomerization. The singular Φ_{cis}/Φ_{trans} ratio found for all the complexes of Scheme I requires that

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[25] The k_A values for the LF ES of $Rh(NH_3)_5I^{2+}$ and $Rh(NH_3)_6^{3+}$ are 6.1×10^8[6d] and 3.3×10^6 s^{-1} (Frink, M.; Ford, P. C. *Inorg. Chem.*, in press), respectively. The respective k_n values are 1.5×10^8 and 4.4×10^7 s^{-1}.

[26] Skibsted, L. H., work in progress.

[27] However, for the $Rh(NH_3)_5CN^{2+}$ ion, NH_3 is labilized from an equatorial site cis to CN^- as expected with this strong-field ligand.[7c,28] In the same context, the *trans*-$Rh(cyclam)(CN)_2^+$ ion is photoinert since cis labilization cannot occur for the cyclam macrocycle.[29]

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the rate constants, k_{ab} and k_{ba}, for equilibration of the two excited-state pentacoordinate intermediates be larger than those for the competing deactivation pathways, k_{na} and k_{nb}, i.e., have values $>10^9$ s^{-1}, a reasonable estimated lower limit for the deactivation rates.[32] In addition, it should be emphasized that the product stereochemical distribution does not simply represent the equilibrium ratio $[SP_b^*]/[SP_a^*]$ but must also include the relative k_n values, i.e.

$$\frac{\Phi_{cis}}{\Phi_{trans}} = \frac{[SP_b^*]k_{nb}}{[SP_a^*]k_{na}} = \frac{k_{ab}k_{nb}}{k_{ba}k_{na}} \qquad (12)$$

Only by assuming that $k_{na} \simeq k_{nb}$ can the Φ_{cis}/Φ_{trans} product ratio be used to infer the relative energies of SP_b^* and SP_a^*.

The photochemistry of the rhodium(III) tetraammine complexes has proved very rich both in terms of photostereochemistry and in terms of ligand effects on excited-state reaction dynamics. The stereochemical lability of these complexes upon photosubstitution of a ligand clearly illustrates the difference between the photosubstitution and thermal substitution mechanisms, and consideration of the fine details provides strong circumstantial evidence for a limiting dissociative pathway as the key step of the photosubstitution mechanism. The application of pulse laser excitation techniques has allowed evaluation of the rates of the ligand substitution (dissociation) from the lowest energy (triplet) excited states of these complexes. For analogous complexes the labilization of a ligand X generally follows the order $H_2O > Cl^- > Br^- > I^-$, perhaps reflecting the relative abilities of these to π bond to an excited-state metal core with a $(d_\pi)^5(d_\sigma)^1$ configuration. Similar π-bonding considerations may explain the inverse order of these ligands in terms of the labilization rates for NH_3 loss. The stereochemical positions of these ligands also have major consequences. With regard to NH_3 substitution, most such labilization in haloammine complexes apparently occurs at a position trans to the halide. In contrast, for dihalo or aquohalo complexes, those having the cis configuration proved to have the greater ES labilities. The opposite is the case for the hydroxohalo complexes. However, both these observations are consistent with the following pattern for the cis and trans pairs $Rh(NH_3)_4XY^{n+}$: The more labile excited-state isomer in each case is also the one that undergoes the greater concomitant isomerization to the final product. A similar apparent coupling of ligand and stereochemical photolability has been reported for the isomers of dihalo trien rhodium(III) complexes.[33] Such observations may suggest some synchronous nature to the ligand dissociation and the isomerization mechanism, a possibility that is not addressed by the mode illustrated in Scheme II.[7a,8a,31] While we remain convinced that this model (or some variation upon the same theme) provides the best existing rationale for the photostereochemistry of the hexacoordinate d^6 complexes, the present excited-state kinetics data do contain clues suggesting a greater coupling of the isomerization and ligand dissociation pathways than implied by this model.

Acknowledgment. This work was supported by grants from the U.S. National Science Foundation to D.M. and to P.C.F., from NATO to L.H.S. and P.C.F., and from the Danish Natural Science Research Council and Carlsberg Foundation to L.H.S. Preliminary studies on some of these systems were carried out by Michael A. Bergkamp[18] at the UCSB laboratories. Rhodium used in these studies was provided on loan by Johnson-Matthey, Ltd.

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(32) For analogous iridium(III) complexes, *cis*- and *trans*-dihalo pairs do not give common product stereochemical distributions, presumably because the higher nonradiative deactivation rates for these heavy-metal complexes are too rapid to allow full equilibration (Talebinasab-Sarvari, M.; Ford, P. C. *Inorg. Chem.* **1980**, *19*, 2640).

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Axial-Ligand-Dependent Electrochemical and Spectral Properties of a Series of Acetate- and Acetamidate-Bridged Dirhodium Complexes

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Received February 24, 1984

Dirhodium complexes, $Rh_2(O_2CCH_3)_n(HNOCCH_3)_{4-n}$ and $[Rh_2(O_2CCH_3)_n(HNOCCH_3)_{4-n}]^+$ (where n = 0–4), were investigated by electrochemical and spectral techniques in nonaqueous media. A uniform variation was observed in the UV–visible spectroscopic properties and the potentials for the first oxidation of $Rh_2(O_2CCH_3)_n(HNOCCH_3)_{4-n}$ upon increasing the number of acetamidate ligands in the dimer or upon changing the nature of the axial ligand and solvent system. Electrochemical data suggest the existence of a π interaction between dirhodium centers and potential π-acceptor ligands such as Me_2SO or PPh_3. EPR spectra of the $[Rh_2(O_2CCH_3)_n(HNOCCH_3)_{4-n}]^+$ complexes suggest a change in the nature of the HOMO of the dirhodium complexes when bridging ligands are substituted for the acetates in $Rh_2(O_2CCH_3)_4$.

Introduction

The electronic structure of dirhodium tetracarboxylate complexes, $Rh_2(O_2CR)_4L_2$, has been a subject of continuing interest, particularly with respect to the nature of the metal–metal bond[2,3] and the mutual effects of metal–metal and metal–ligand interactions.[4-8] Recently, the synthesis and characterization of dirhodium(II) complexes with bridging ligands containing different kinds of donor atoms has been reported, and the electronic structure of these kinds of com-

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